NASA TECHNICAL NOTE

NASA TN D-4862

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THE ROLE OF CHEMICAL REACTIONS
IN THE MECHANISM OF COMMINUTION
OF DUCTILE METALS INTO
ULTRAFINE POWDERS BY GRINDING

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • OCTOBER 1968

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ABSTRACT

On grinding in pure water, zirconium, tantalum, iron, and stainless-steel powders were extensively comminuted and simultaneously oxidized with hydrogen release, whereas nickel, copper, and silver powders did not react with water and their particle sizes increased. On grinding nickel, copper, and silver in water pressurized with oxygen, nickel and copper became extensively comminuted and were oxidized, whereas silver did not react with oxygen and its particle size increased. From these results and other considerations, it is hypothesized that for extensive comminution of ductile metals and alloys to occur on grinding they must react with the grinding media.

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SUMMARY

This investigation was conducted to determine the behavior of metal powders on ball milling either in water or in oxygenated water and thereby gain an insight into the grinding mechanism. Zirconium, tantalum, iron, and an alloy (type 430 stainless steel) became extensively comminuted when they were ball milled in pure water. They also reacted with water during ball milling, and hydrogen was released. Nickel, copper, and silver could not be comminuted by ball milling in pure water. On the contrary, the average particle size of these powders increased, because of particle welding. None of these metals reacted with water during ball milling.

Nickel, copper, and silver were also ball milled in oxygenated water. Nickel and copper became extensively comminuted during ball milling and reacted with the dissolved oxygen. Silver neither reacted with the dissolved oxygen nor was it comminuted. On the contrary, the average particle size of the silver powder increased.

X-ray diffraction analyses of the powders that could be comminuted by ball milling showed the presence after comminution of either oxides, hydroxides, or (for zirconium and perhaps for tantalum) hydrides. X-ray diffraction analyses of the powders that could not be comminuted showed only the pure metal.

From the preceding results and from other considerations, it is hypothesized that for extensive comminution to occur in a reasonable time during ball milling, the metal or alloy must react chemically with the grinding medium.

INTRODUCTION

Ultrafine metal and alloy powders are finding an ever growing number of applications in metallurgy and in other fields (ref. 1). Of particular interest are ultrafine metal and

alloy powders suitable for dispersion strengthening (refs. 2 and 3). Various research programs on dispersion strengthening are being conducted and in some of these programs the ball-milling method is being used to produce dispersion-strengthened materials. This method usually involves the simultaneous grinding of a metal or alloy and a dispersoid followed by consolidation of the resulting powder mixture. To obtain the ultrafine powders required for dispersion strengthening (ref. 2), grinding is performed in many liquids, with or without grinding aids (refs. 4 and 5). Nonaqueous liquids usually contain water as an impurity and some grinding aids may contain water of hydration (ref. 5). The water present may affect the grinding process.

The writer has shown (ref. 6) that on ball milling chromium in water, the chromium is oxidized, and hydrogen is released. It was surmised that the same reaction may occur on ball milling other metals and alloys in water-bearing liquids. Therefore, the investigation of ball milling in water was extended to metals and alloys other than chromium. In the course of the investigation, however, it became apparent that the data, together with the results from a few additional experiments, could be used to postulate a comminution mechanism for ductile metals and alloys.

A well-known comminution theory is that of Smekal (ref. 7). According to this theory, comminution is possible because of the weakening effects of surface cracks and other imperfections in materials. This theory imposes a lower limit of about 1 micrometer for the ground particles.

The beneficial effects of liquids and additives on the rate of grinding are well known (ref. 8). Mechanisms by which liquids and additives may aid in grinding were reviewed by Rose and Sullivan (ref. 8). One aspect of these effects is based on Rehbinder's theory of crack propagation in materials under stress (ref. 9). According to Rehbinder's theory, liquids or additives may promote the spread of cracks in stressed materials by lowering the surface tension at the crack tip. Rose and Sullivan surmise that the same mechanism may be operative during grinding, thereby facilitating comminution of the particles. In addition, Rose and Sullivan reviewed how additives may act as dispersants as a result of their being adsorbed on the surface of the particles being ground. This concept has been suggested by Quatinetz, Schafer, and Smeal (ref. 5) to explain from their experiments the major role of additives that enabled them to grind metals down to 0.1 micrometer. Discussions of other comminution theories and additional sources of material on the subject are given in reference 10. None of these previous suggestions and theories, however, can account for all phenomena encountered during ball milling of metals to submicron size in this and in a previous investigation by the author (ref. 6).

The objectives of this investigation were to determine the behavior of metal powders during ball milling either in pure water or in oxygenated water and to gain an insight into the grinding mechanism.

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Zirconium, tantalum, iron, nickel, copper, and silver powders were ball milled in pure water. These metals were selected because their oxides cover a wide range of free energy of formation. For comparison purposes, an alloy (type 430 stainless steel) was also ball milled in pure water. The pressure of the hydrogen released during ball milling was monitored in order to determine the oxygen that combined with the metal or alloy.

In order to obtain more information on the nature of the grinding process, nickel, copper, and silver powders were also ball milled in oxygenated water (water pressurized with oxygen). The oxygen that reacted with the powders was determined from the pressure decrease in the mills.

The powders resulting from ball milling in pure water and in oxygenated water were subjected to surface area, optical microscopy, and X-ray diffraction analyses. With these data, the oxygen calculated to be combined with the metals during ball milling, and comparison of the free energies of formation of the oxides of the milled powders with that of water, a comminution mechanism was postulated.

MATERIALS, EQUIPMENT, AND PROCEDURES

The materials used in this investigation were powdered metals, deaerated distilled water, high-purity helium, and commercial grade (99.5 percent purity) oxygen. The powdered metals used were zirconium, tantalum, iron, nickel, copper, and silver. A 16 percent chromium, ferritic stainless steel, type 430, was also used. The purities (or nominal compositions) and the surface areas of these metals and the alloy are given in table I.

Aluminum and magnesium were also considered for use in this investigation. However, a preliminary investigation revealed that the powders of these two metals reacted with water (with the release of hydrogen) without grinding. Since this investigation is based on the monitoring of the release of hydrogen during grinding, aluminum and magnesium were not used.

Ball Mills and Balls

The type of ball mill used in this investigation is shown in figure 1. The mills were made from type 410 (12 percent chromium) stainless steel, have an inside diameter of 10.2 centimeters and a volume of 1580 cubic centimeters. Their covers have O-ring gaskets to provide a gas-tight seal. The mill pressure was monitored with a 7.5-centimeter-diameter gage mounted on the cover. This gage was demountable so that gages covering different pressure ranges (including vacuum) can be used. They were

TABLE I. - MATERIALS

Material	Manufacturer's specifications	Specific surface area,[a] m^2/g	Average particle size,[b] μm
Zirconium	99+ percent zirconium	0.10	6.25
Tantalum	99.5 percent tantalum	.64	.43
Chromium[c]	99.9 percent chromium (electrolytic flake)	.12	4.63
Iron	99.84 percent iron, 0.09 percent carbon (carbonyl iron)	.38	1.34
Stainless steel, type 430	16 percent chromium (nominal), 0.12 percent carbon, remainder iron	.38	1.36
Nickel	99.8 percent nickel	.50	.90
Copper	99.9 percent copper (hydrogen cleaned before use)	.14	3.20
Silver	99.5+ percent silver	.28	1.36

[a] Determined by BET method (ref. 11).
[b] Determined from formula (ref. 2), particle size (μm) = $4/\rho S$, where ρ is density (g/cm^3) and S is specific surface area (m^2/g) of material.
[c] Data from ref. 6.
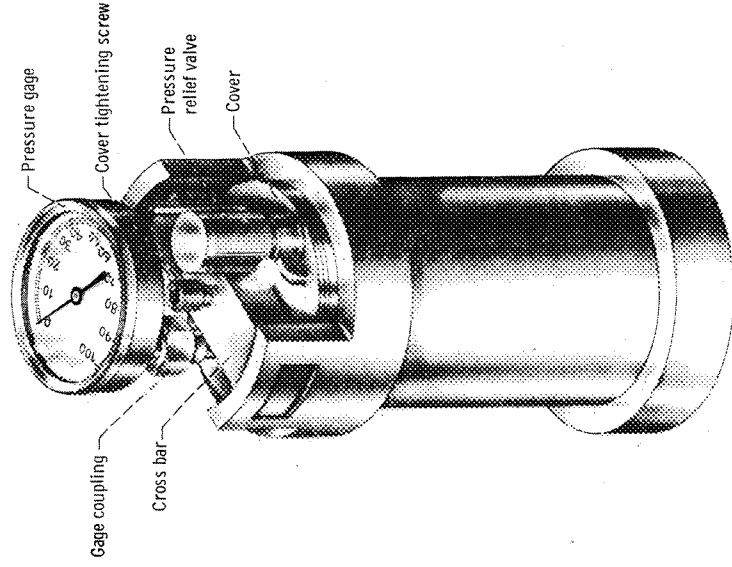
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Figure 1. - Gas-tight mill with pressure gage.

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calibrated with a master gage to an accuracy of better than 1/2 percent of full-scale reading. The mills also have a vacuum-type valve which was used either to relieve excess pressure, to pressurize the ball mill, or to evacuate it as required during the various operations to be described.

The balls used for ball milling were 12.6 millimeters (nominal) in diameter and made from type 440 (17 percent chromium, martensitic) stainless steel. In all runs, 400 of these balls were used. Each batch of balls weighed approximately 3220 grams and was weighed with an accuracy of ±0.01 gram.

Ball Milling With Pure Water

In some runs (table II), the powders were ball milled with pure water as the grinding medium. For these runs, the ball mill was loaded with 150.00±0.01 grams of one of the metals and 750±2 cubic centimeters of distilled water. The free volume of the mill was about 402 cubic centimeters. The ball mill was evacuated with a mechanical vacuum pump to cause the water to boil and thereby remove dissolved gases from the water. The ball mill was then pressurized with high-purity helium and checked for leaks with a mass-spectrometer-type leak detector. The ball-mill (helium) pressure was then adjusted to slightly above atmospheric pressure, and the ball-milling run started.

In all the experiments, the ball mills were run at 100 rpm. Pressure readings were taken at regular milling time intervals. The ball-mill pressures were released as required so as not to exceed the pressure range of the gages being used. Pressure readings were continued for some time after the end of each ball-milling run. The bulk of the water was then removed either by decantation or by centrifuging. The moist powder was dried by evacuation. The dried powders were handled inside a helium-filled glove box. Powder samples for surface area determination were taken. Also, at the end of each run, the balls were cleaned and weighed again with an accuracy of ±0.01 gram. This was done in order to determine the pickup (or increase in powder weight due to wear of balls and mills).

Ball Milling in Water Without Powder Charge

In one experiment, the ball-milling run was begun without any powder in the mill. The other ball-milling conditions were the same as for ball milling with powders and with pure water described previously. Pressure readings were taken during the run. At the end of the run, the ball mill was opened in a helium-filled glove box. The liquid from the mill was loaded in gas-tight containers and centrifuged. The recovered powder (produced

TABLE II. - TEST RESULTS OF COMMINUTED METAL POWDERS AND FREE ENERGY OF FORMATION

OF METAL OXIDES AND OF WATER

Material	Initial particle size, μm [a]	Powders ball milled in pure water				Powders ball milled in water pressurized with oxygen				Formula	Oxides or hydroxides [c] Standard free energy of formation at 298°C, cal/(g-atom oxygen)
		Time, hr	Oxygen content, $\frac{g\ oxygen}{g\ metal}$	Surface area, m²/g	Calculated particle size, μm [b]	Time, hr	Oxygen content, $\frac{g\ oxygen}{g\ metal}$	Surface area, m²/g	Particle size, μm [b]		
Zirconium	6.25	384	0.059	12.1	0.052	-----	------	------	-----	ZrO_2	-123 900
Tantalum	0.43	384	0.048	4.42	0.062	-----	------	------	-----	Ta_2O_5 TaO_x	-91 300 -91 300 · x (approximately)
Chromium [d]	4.63	384	0.064	9.65	0.058	-----	------	------	-----	Cr_2O_3 CrO_2 CrO_3	-84 400 -65 000 -40 300
Iron	1.34	38	0.015	3.55	0.14	-----	------	------	-----	FeO $FeO \cdot Fe_2O_3$ Fe_2O_3	-58 670 -60 800 -59 100
430 Stainless steel	1.36	384	0.14	83.8	0.0065	-----	------	------	-----	$FeO \cdot (Fe, Cr)_2O_3$	-60 800 [e] (approximately)
Nickel	0.90	174	0	0.99	0.45	174	0.092	7.72	0.058	NiO $Ni(OH)_2$	-50 600 -54 150 [f]
Copper	3.20	205	0	0.096	4.7	52.5	0.12	36.4	0.012	Cu_2O CuO	-35 450 -30 850
Silver	1.36	237	0	0.16	2.4	237	0	0.060	6.4	Ag_2O Ag_2O_2	-2 500 3 300
Water	----	---	------	------	------	-----	-----	------	------	H_2O	-56 720

[a] From table I.

[b] Calculated from formula (ref. 2), particle size (μm) = $4/\rho S$, where ρ is density (g/cm³) and S is specific surface area (m²/g) of material.

[c] Data from ref. 20, except as noted.

[d] Data from ref. 6.

[e] This ΔF was assumed to be the same as that of $FeO \cdot Fe_2O_3$.

[f] Data from ref. 21.

by the rubbing action of the balls with each other and with the mill) was dried under vacuum and then weighed under helium cover. Some of this powder was loaded in a capillary tube in the helium-filled glove box and the capillary tube sealed. This powder sample was used for X-ray diffraction analysis. The powder obtained by wear of the balls was determined by weight loss. The powder obtained by wear of the ball mill was considered to be the increase in weight of the powder less the weight lost by the balls (after corrections for the oxygen combined with the powder during ball milling).

Ball Milling With Oxygenated Water

In some runs (table II), the ball mills were evacuated and then pressurized with oxygen after the ball mills were leak checked with helium. For these runs, the water used was adjusted to make the free volume of the mill 500±2 cubic centimeters. The other ball-milling conditions (i.e., mill speed, weight of balls, and powder charge) were the same as for ball milling in pure water. Also, as for runs with pure water, pressure readings were taken at regular intervals after cooling the mills. The ball mills were repressurized with oxygen to maintain a pressure above atmospheric.

Examination of Powders

The surface areas of both the as-received and ball-milled powders were determined by the BET method (ref. 11).

Some of the ball-milled powders were flake shaped. These flakes were mounted edgewise for metallographic examination. To do this, the flakes of each metal to be examined were first mixed with thermosetting resin mounting powder and pressed into thin disks. Each disk was cut axially, and a piece, placed on edge, was again pressed with mounting powder. In this manner, the cross section of the disk showed in the photomicrographs. For comparison, as-received powders of the same metals were mounted in the same manner for metallographic examination, even though they were not flake shaped.

Powders for X-ray diffraction analyses were loaded, in a helium-filled glove box, into capillary tubes and the tubes then sealed with vacuum grease. The powders were loaded while still moist to prevent possible loss of water of hydration.

RESULTS

Wear of Balls and Mill in Run Without Powder

A 262-hour ball-milling run was made without any powder charge to determine the pickup. The pickup is defined as the powder formed by wear of balls and mill. Hydrogen was generated at a constant rate, as determined by the pressure increase in the ball mill. From this and other factors, it was concluded that the pickup rate from balls and mill was also constant.

The pickup from the balls alone, determined from the weight lost by the balls during the run, was 1.81×10^{-3} grams per hour. The fact that hydrogen was released during ball milling meant that the powder formed (pickup) was being oxidized by reaction with water (ref. 6). Hence, the total amount of material removed from balls and mill was calculated by subtracting the weight of the oxygen (calculated from the buildup in hydrogen pressure) reacted with the powder from the total weight of the powder determined after ball milling. The combined pickup rate from balls and mill was calculated to be 2.53×10^{-3} grams per hour. This figure is equivalent to 1.40 times the pickup rate from balls alone.

The weight of the oxygen reacted with the powder used in the preceding calculations was determined by the method described in the appendix.

X-ray diffraction analysis of the powder picked up from balls and mill showed that this powder consisted of alpha iron and the spinel ferrous oxide – ferric oxide $(FeO \cdot Fe_2O_3)$. The balls and mills, however, were made from stainless steel. For this reason, it was deduced that the pickup was the mixed spinel $(FeO) \cdot (Fe, Cr)_2O_3$ and ferritic stainless steel.

In runs where powders were milled, the amount of hydrogen generated by the pickup can be estimated from the weight lost by the balls during the ball-milling run, since, as already stated, the total pickup is 1.40 times this value. Only in pure water runs with nickel, copper, and silver where the increase in pressure was very small (less than 0.5 atm (0.5×10^5 N/m^2)) was a correction for the hydrogen generated by the pickup applied.

Ball Milling in Pure Water

The surface areas and particle sizes of all the metals and the alloy ball milled in pure water are shown in table II. Of the metals and the alloy milled in pure water, zirconium, tantalum, stainless steel, and iron were extensively comminuted, whereas nickel, copper, and silver were not. The term "extensive comminution" will be used repeatedly in this report and for this reason its meaning will be clarified before proceeding any further.

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Table II shows that tantalum, zirconium, chromium, iron, and stainless steel ball milled in pure water have particle sizes ranging from about 1/7 to 1/200 the particle sizes of the original powders. No doubt longer ball-milling time of these materials would produce still finer powders, since hydrogen evolution (which is related to comminution) was still continuing at an undiminished rate at the end of each run. This type of comminution in which metal and alloy powders can be reduced to very fine submicron size powders much smaller than the original powder is what is meant by "extensive comminution." In contrast, the particle sizes of copper and silver ball milled in pure water (see table II) show that these two materials actually agglomerate during ball milling. It will be shown later that the apparent reduction in particle size on ball milling nickel in pure water (table II) results from flattening of the particles without any appreciable comminution.

The plots of the hydrogen pressure developed during ball milling some of the metals are shown as a function of ball-milling time in figures 2 to 6.

The hydrogen pressure developed on ball milling zirconium in pure water is shown as a function of milling time in figure 2. The breaks in the curve indicate the points at which the hydrogen pressure was released. The flat portion of this curve is probably caused by formation of zirconium hydride during ball milling (shown later). Similar curves were obtained on ball milling tantalum and (except for the flat portion) stainless steel in pure water. The corresponding curve for chromium obtained in a previous investigation by the writer (ref. 6) is also similar.
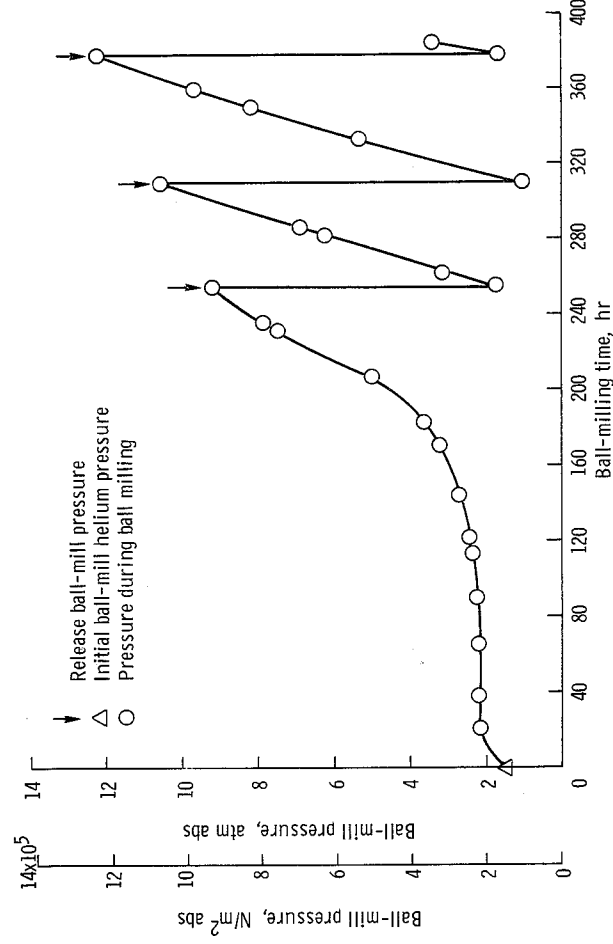

Figure 2. - Hydrogen pressure developed on ball milling zirconium in pure water.
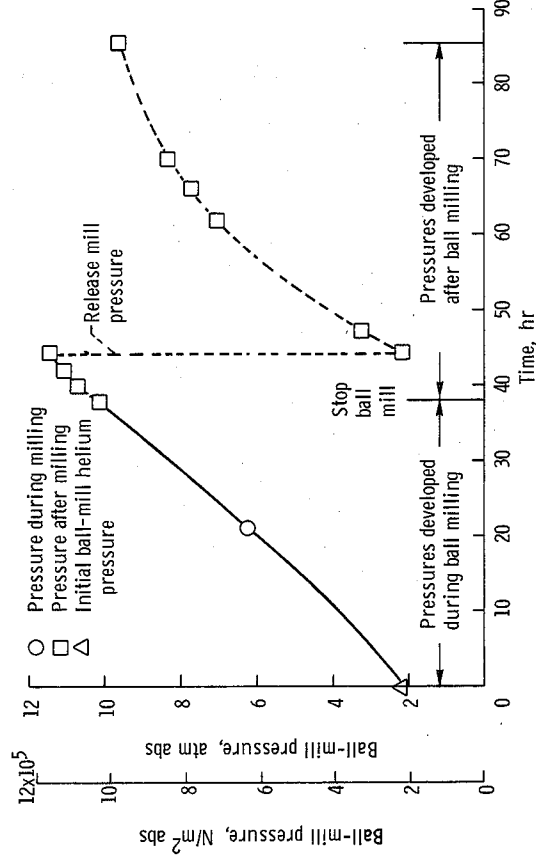
Figure 3. - Hydrogen pressure developed during and after ball milling iron in pure water as function of time.

TABLE III. – HYDROGEN GENERATION BEFORE AND AFTER END OF BALL MILLING

Material	Duration of milling run, hr	Just before end of run	Time elapsed, hr	After end of run			Ratio of rate of hydrogen generation just before end of ball milling to that after ball milling, R_1/R_2
		Rate of hydrogen generation, moles/hr, R_1		Ball-mill pressure		Rate of hydrogen generation, moles/hr, R_2	
				atm abs	N/m² abs		
Chromium[a]	48	350×10^{-6}	48	1.95	1.97×10^5	1.0×10^{-6}	350
	768	1230	100	6.77	6.86	9.38	131
Type 430 stainless steel	384	2630×10^{-6}	24	5.68	5.76×10^5	404×10^{-6}	6.5
			40	3.72	3.77	528	5.0
			206	4.33	4.39	250	10.5
Tantalum	384	1830×10^{-6}	24	4.15	4.21×10^5	81×10^{-6}	22.7
Zirconium	384	3670×10^{-6}	24	3.35	3.40×10^5	357×10^{-6}	10.3
Iron	38	8900×10^{-6}	2	10.2	10.34×10^5	4540×10^{-6}	1.92

[a]Data from ref. 6.

On ball milling nickel, copper, and silver in pure water, only a very slight (less than 0.5 atm (0.5×10^5 N/m^2)) increase in ball-mill pressure occurred. This increase in pressure was accounted for by the reaction of the stainless steel picked up from balls and mills (mentioned previously). Hence, nickel, copper, and silver did not react with water during ball milling. The corrected-pressure - milling-time plots are shown in figures 4 to 6. Since there was no hydrogen evolved during these runs (except from the reaction with the pickup), the plots are horizontal.

The mill pressure as a function of ball-milling time developed on milling iron in pure water is shown in figure 3. Pressure readings were continued after the end of a 38-hour ball-milling run. As shown in figure 3, hydrogen generation continued after the mill was stopped. Because of the large amounts of hydrogen evolved after stopping the ball mill, the ball-milling run with iron was discontinued. To a greater or lesser extent, all the metals and the alloy used in this investigation as well as chromium (ref. 6) which release hydrogen on ball milling in pure water continue to do so after milling is stopped.

In view of this, it may be questioned what proportion of the hydrogen evolved in each of the runs (where this evolution occurs) is simply reaction with water which would occur without grinding. The "after-ball-milling" hydrogen release for these metals and the alloy is shown in table III, as calculated from equation (A1). Comparison of these after-ball-milling hydrogen releases for the various metals and the alloy is facilitated by the ratios R_1/R_2 shown in table III, where R_1 is the rate of hydrogen generation just before the end of the ball-milling run and R_2 is the rate of hydrogen generation just after the end of the run. This ratio indicates that the rate was higher during ball milling and suggests that in most cases the hydrogen evolution is the result of reaction with new surfaces created during ball milling.

As shown in table III for stainless steel and in figure 3 for iron, the rate of hydrogen evolution for these two materials appears to be both pressure and time dependent. The evidence of pressure dependence may be seen in figure 3 by noting the change in slope of the pressure-time plot immediately after releasing the pressure at 44 hours. The evidence for time dependence may be seen in figure 3 by comparing slopes between about 40 and 44 hours with those between 70 and 85 hours. Despite the lower mean pressure (about 9 atm or 9×10^5 N/m^2) corresponding to the slope of the curve between 70 and 85 hours, this slope is smaller than the one between 40 and 44 hours (11 atm or 11×10^5 N/m^2) thus indicating a time dependence.

Ball Milling in Oxygenated Water

As already indicated, nickel, copper, and silver did not react with water during ball milling. To determine whether there was any relation between the milling medium and
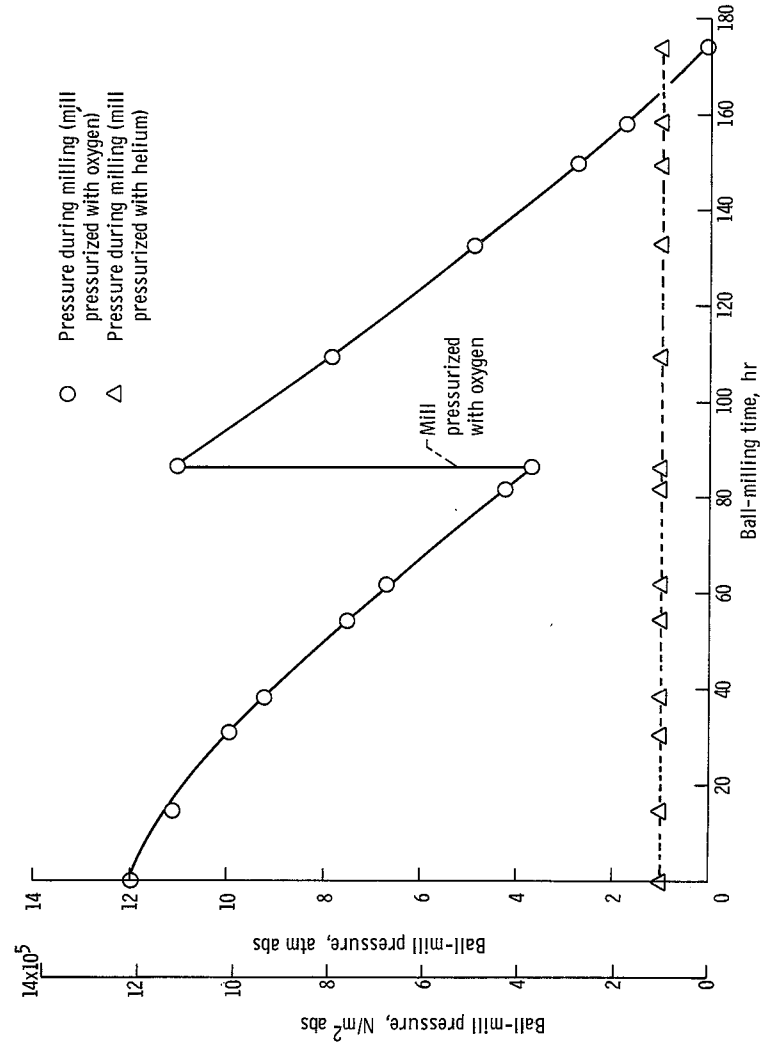
Figure 4. – Pressure change on ball milling nickel in water as function of milling time.
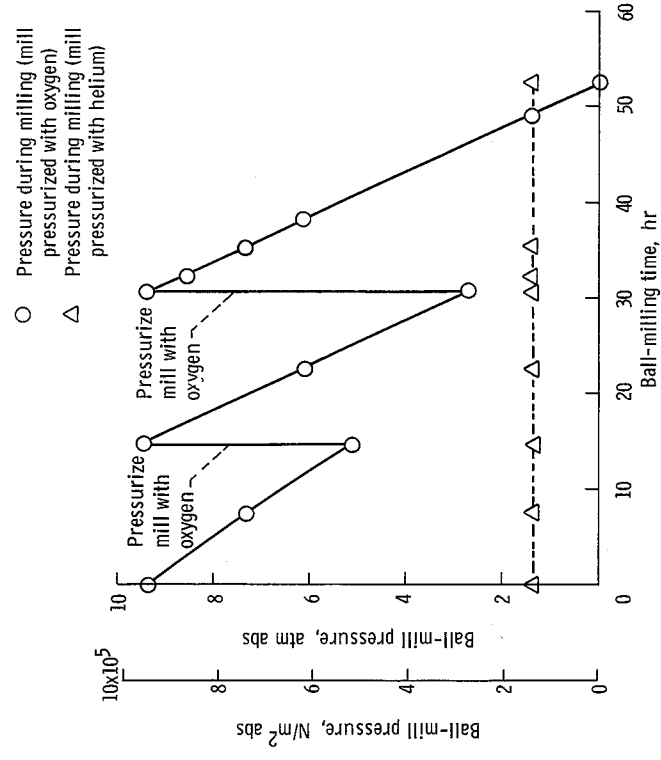
O   Pressure during milling (mill pressurized with oxygen)

△   Pressure during milling (mill pressurized with helium)

Mill pressurized with oxygen

Ball-milling time, hr

Ball-mill pressure, atm abs

Ball-mill pressure, N/m^2 abs

Figure 5. – Pressure change on ball milling copper in water as function of milling time.

O   Pressure during milling (mill pressurized with oxygen)

△   Pressure during milling (mill pressurized with helium)

Pressurize mill with oxygen

Pressurize mill with oxygen

Ball-milling time, hr

Ball-mill pressure, atm abs

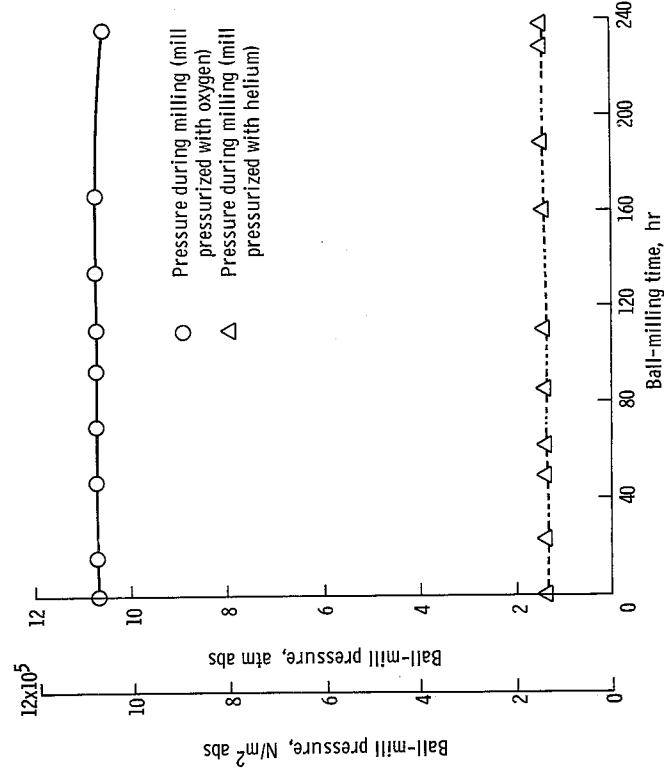Ball-mill pressure, N/m^2 abs

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Figure 6. - Pressure change on ball milling silver in water as function of milling time.

comminution, these three powders were ball milled in oxygenated water (water pressurized with oxygen). The surface areas and particle sizes of the nickel, copper, and silver powders obtained by ball milling in oxygenated water are shown in table II. The particle sizes of the original powders are shown in the first column of this table. Nickel and copper were extensively comminuted, whereas silver was not. The oxygen pressures in the ball mills as a function of ball-milling time for nickel, copper, and silver are shown in figures 4, 5, and 6, respectively. The breaks in the curves of figures 4 and 5 indicate the points at which the mills were repressurized with oxygen. It should be noted that the last point in each of these two curves is at nearly 1 atmosphere (1.0×10^5 N/m^2) below atmospheric pressure (i. e., good vacuum).

After ball milling silver in oxygenated water, it was noticed that the balls and the inside of the ball mill had a brownish layer of oxide. The balls showed a slight increase in weight after ball milling. This oxidation of the balls and the mill would account for the slight decrease in oxygen pressure shown in figure 6.

Miscroscopic Examination of As-Received and Ball-Milled Powders

Microscopic examination of the as-received metal powders used in this investigation showed them to be approximately equiaxed. The surface areas and particle sizes (0. 43 to 6. 2 μm) of these as-received powders are shown in table I.

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Ball-milled powders of zirconium, tantalum, iron, and stainless steel were too fine (0.0065 to 0.14 μm) to be conveniently examined with the optical microscope by the specimen mounting technique used for silver, nickel, and copper described in the section MATERIALS, EQUIPMENT, AND PROCEDURES. On the other hand, this mounting technique is not suitable for mounting submicron size powders for edgewise electron microscopy examination. Since chromium forms flakes during ball milling (ref. 6), it is surmised that these very fine powders of zirconium, tantalum, iron, and stainless steel are probably also flake shaped.

Unusually large flakes were obtained by ball milling silver in pure water. A photomicrograph of part of one of these silver flakes is shown in figure 7. For comparison purposes, photomicrographs of as-received silver powder, and silver ball milled in oxygenated water are also shown in this figure.

Although smaller than the silver, the powder particles obtained by ball milling nickel and copper in pure water are also flake shaped. Photomicrographs of nickel and copper powders ball milled in pure water together with those of the corresponding as-received powders are shown in figures 8 and 9, respectively. As shown in table II, the particle
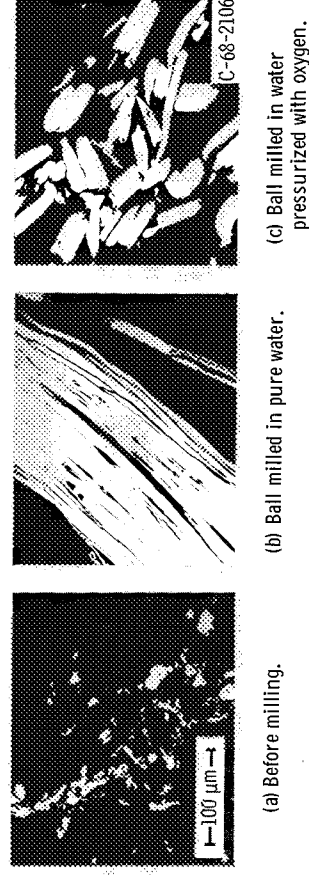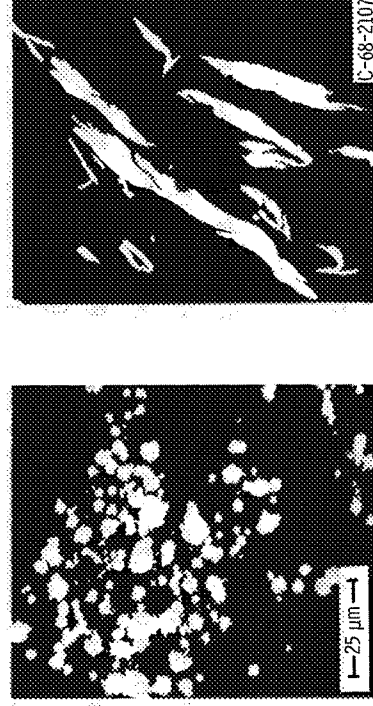

(a) Before milling.   (b) Ball milled in pure water.   (c) Ball milled in water pressurized with oxygen.
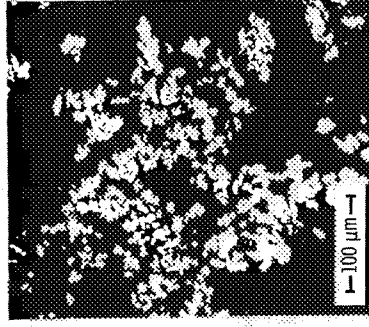
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Figure 7. - Photomicrographs of silver powder. Dark background is metallographic mount. Unetched.

(a) Before milling.   (b) Ball milled in pure water.

C-68-2107

Figure 8. - Photomicrographs of nickel powder. Dark background is metallographic mount. Unetched.

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(a) Before milling.   (b) Ball milled in pure water.

C-68-2108

Figure 9. – Photomicrographs of copper powder. Dark background is metallographic mount. Unetched.

TABLE IV. – RESULTS OF X-RAY DIFFRACTION ANALYSES

Metal or alloy powder	Ball-milling conditions	Phases revealed by X-ray diffraction	Remarks
Copper	Pure water	Cu (only)	
	Oxygenated water	Cu CuO Cu_2O (weak)	
Nickel	Pure water	Ni (only)	
	Oxygenated water	Ni $Ni(OH)_2$ NiO (weak)	
Zirconium	Pure water	ZrO_2 ZrH α-Fe	α-Fe is actually stainless steel picked up from balls and mill
Tantalum	Pure water	Either TaH or TaO_x	Broad diffraction lines preclude definite identification
Iron	Pure water	α-Fe Fe_3O_4 (spinel)	
430 Stain-less steel	Pure water	Fe_3O_4 δ-FeO(OH) α-Fe	Partial replacement of Fe^{+3} by Cr^{+3} in oxides and/or hydroxides of iron would give a similar pattern

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sizes of the nickel and copper powders ball milled in oxygenated water are 0.058 and 0.012 micrometer, respectively. These particle sizes are too small to be examined with the optical microscope.

X-ray Diffraction Analyses

The results of X-ray diffraction analyses of most of the ball-milled powders are shown in table IV. Silver was not analyzed because of the large size of the silver flakes. By comparison with the results for nickel and copper when they did not react with the grinding medium, however, it can be assumed that the only phase present was silver.

DISCUSSION OF RESULTS

Comminution of Powders in Pure Water - Thermodynamic and Other Considerations

The behavior of the metals that reduced in size and those that did not become extensively comminuted on ball milling in pure water can be explained from thermodynamic considerations.

The standard free energies of formation ΔF^O of the oxides of the metals used in this investigation are shown in table II. The standard free energy of formation of water is also included in this table for comparison purposes. Comparing the data in table II with ΔF^O values shows that only the metals whose oxides have a more negative ΔF^O than water released hydrogen on ball milling in pure water. The release of hydrogen would be expected to occur according to the chemical equations

$$xM(s) + yH_2O(l) = M_xO_y(s) + yH_2(g) \tag{1}$$

or

$$M(s) + zH_2O(l) = M(OH)_z(s) + \frac{z}{2} H_2(g) \tag{2}$$
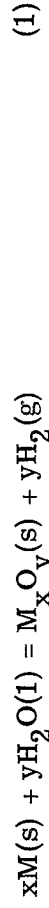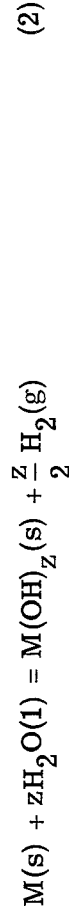
According to thermodynamic principles, the preceding reactions can take place only if the free energy changes for the reactions are negative. However, thermodynamics is not the only criterion that must be considered. Usually, even if the free energy change is negative, most metals do not react with water to any appreciable extent. The reason

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the reactions of these metals with water do not occur readily is that most metals are covered with a layer of oxide or chemisorbed oxygen that prevents it. In some metals (like lithium) the oxide layer is water soluble and after this layer is dissolved reaction can take place readily. However, other metals like aluminum, for instance, may form hydrated oxides or hydroxides with water which, although not soluble in water, may crack or spall off during grinding and thus expose the metal to continued attack.

It can be shown thermodynamically that the hydrogen pressures built up in the mills where reaction occurred are too low to reverse the reactions. Thus, for the reaction of water with iron to form ferrosoferric oxide (FeO · Fe_2O_3), the equilibrium hydrogen pressure was calculated to be about 10^{45} atmospheres (10^{50} N/m^2). The corresponding hydrogen equilibrium pressure for stainless steel is at least equal to that for iron, and for zirconium and tantalum the pressure is much higher.

As described earlier, comparison of the R_1/R_2 ratios and pressure data in table III (and in fig. 3 for iron) show that the rate of hydrogen generation after the ball mills are stopped can be both pressure and time dependent. The reasons why this after-ball-milling pressure increase can be both pressure and time dependent will be explained later.

It has been shown in a previous investigation by the writer (ref. 6) that the oxide layer formed on chromium powder ball milled in water is about two chromic oxide (Cr_2O_3) molecules thick. Similar oxide layers would be expected to form in the metals that react with water during ball milling. Whether these oxide layers are formed by a bulk or suface diffusion mechanism, the diffusion is time dependent. Hence, the rate of after-ball-milling hydrogen evolution can be expected to be time dependent. Again, as the coverage of the metal particles by their oxides increases toward an equilibrium value, the activity of the metal in equation (1) decreases. Hence, the equilibrium hydrogen pressure also decreases. The previously mentioned change in slope at 44.5 hours in figure 3 is an example of pressure dependence of hydrogen evolution. The data for stainless steel in table III are an example of the time dependence of the rate of hydrogen evolution.

To a greater or lesser extent, all the other metals that reacted with water show the same kind of time and pressure dependence of the rate of after-ball-milling hydrogen evolution. These effects though they may be present, probably cannot be observed during ball milling because, as shown in table II, except for iron, the rate of hydrogen evolution during ball milling is much larger than after ball milling. The behavior of iron may be a result of the formation of a spinel layer (by reaction with water) which is either porous or cracks during formation.

In addition to releasing hydrogen by their reaction with water, metals that reacted with water were affected differently during ball milling than the metals that did not react with water. As shown by comparison of tables I and II, all the metals that reacted with water during ball milling also had their surface areas considerably increased. These are

zirconium, tantalum, iron, and stainless steel. Chromium (ref. 6) behaved in the same manner. On the other hand, copper and silver did not react with water on ball milling and, as shown by comparison of tables I and II, the surface areas of copper and silver decreased considerably during ball milling. Despite the flattening of silver and copper into flakes (shown in fig. 7(b) and 8(b)), the welding of these flakes into larger ones caused a decrease in surface area. Nickel does not react with water during ball milling either. Although nickel shows a slight increase in surface area on ball milling in pure water (see tables I and II) this increase results from flattening of the particles rather than from comminution, as comparison of figures 9(a) and (b) show. In summary, the metals and alloys that reacted with water during ball milling were extensively comminuted. On the other hand, the metals that did not react with water during ball milling were not comminuted. On the contrary, the milling caused the powder particles to grow in size.

Ball Milling in Oxygenated Water

The results of ball milling in oxygenated water confirm what was observed on ball milling in pure water: that those metals that were extensively comminuted were those that reacted chemically with the milling medium. The reactions (as in the case of ball milling with pure water) are consistent with thermodynamic principles. Table II shows that the standard free energies of formation of the oxides of nickel, copper, and silver (Ag_2O) are negative. Hence, the reaction of these metals with oxygen is possible. For silver, however, the standard free energy of formation of silver oxide (Ag_2O) is relatively small and probably the reaction rate is too slow to affect the grinding characteristics of the powder.

Generalizations on Chemical Effects

The only significant difference between the two ball-milling media (pure water and oxygenated water) used in this investigation was their reactivity toward the metals being milled. As clearly shown by the experimental results, extensive comminution required reaction between the metal and the ball-milling medium. It was also shown that the observed reactions were consistent with thermodynamic principles. In addition, the author has observed (in other experiments not described here) that on ball milling metals in a variety of pure liquids (acetone, alcohol, methylene chloride, toluene, etc.), the finer the metal powder obtained by ball milling the greater their contamination with elements originating in the ball-milling liquid. From all these observations it is hypothesized that for extensive comminution of metals and alloys to occur during grinding they must react

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with the grinding medium. Considering that bare metal surfaces weld readily (ref. 12), this hypothesis must be qualified with the proviso that the reaction product be retained as a coating on the particles being milled. Even with this proviso, however, and because of the many factors affecting the grinding process (ref. 8) there may be exceptions to this rule. The hypothesis stated, however, is believed to have general validity.

Microstructure of Ball-Milled Powders

The nature of the particles shown in figure 7 to 9 indicate the manner by which particles may grow (or their surface areas decrease) during ball milling. The fines in the as-received silver, nickel, and copper powders (figs. 7(a), 8(a), and 9(a), respectively) disappeared on ball milling in pure water. In all cases, the fines were flattened into flake-shaped particles and these flakes welded into flake-shaped agglomerates (figs. 7(b), 7(c), 8(b), and 9(b)). It appears that on ball milling silver in oxygenated water, the flake shaped agglomerates were broken after they reached a certain size.

The surface area of the silver powder ground in pure water was higher than that ground in oxygenated water (table II). The reason for this difference could be that (as shown in fig. 7(b)) the individual flakes in the agglomerates formed by ball milling in pure water were thinner and more loosely bonded (probably because of the very large size of the agglomerates) than those formed by ball milling in oxygenated water (fig. 7(c)). Hence, since the BET method of surface determination measures the exposed surface, the silver ball milled in pure water showed a larger surface area.

In figures 7(b), 8(b), and 9(b), the pores or pockets at the interfaces between the individual flakes making up the agglomerates can be noted. Although generally too small to be seen under the microscope by presently available techniques, it is surmised that on welding submicron size particles during grinding, the same kind of pores or pockets form. These pores or pockets would probably be filled with the ball-milling medium. This trapped ball-milling medium could cause contamination of the powders beyond that caused by reaction.

Because ductile metal powders can form flakes and weld during ball milling, it is surmised that if mixtures of very fine metal powders and dispersoids were ball milled in a nonreactive grinding medium the dispersoid would be trapped at the interface between flakes. This might prove a good method of obtaining uniform mixtures of dispersoids in metal powders (for dispersion strengthening or other applications) in some systems.

Mechanism of Comminution of Metals and Alloys

The experimental evidence gathered in this investigation and discussed in the preceding pages shows that extensive comminution of ductile metals during ball milling occurred only when the metal reacted with the ball-milling media. When there was no reaction between the metal powder and ball-milling medium, the particles grew in size by welding onto each other (figs. 7 to 9). There is also experimental evidence (ref. 13) showing that welding of particles can occur concurrently with comminution. These experimental facts will be used in the arguments that follow in an attempt to describe the comminution mechanism of ductile metals and alloys during ball milling.

As indicated by the results just discussed, there are two competing processes proceeding concurrently during ball milling. These two processes are the fracturing of large particles into smaller ones and the welding of particles into larger ones as they agglomerate and are impacted together. Since the main purpose of ball milling is to reduce the particle size of the ball-milled powder, it follows from the preceding discussion that this purpose can be accomplished by increasing the particle fracture rate and by decreasing the welding rate. These two processes and the various factors affecting them are discussed here in some detail. The discussion, however, is centered around the chemical aspects of the grinding process as experimentally verified in (or as surmised from the experimental results of) this investigation.

Fracture of particles during ball milling. - If a brittle material such as glass is hammered it can be readily pulverized, whereas ductile metals such as iron can be fractured in this manner only with great difficulty. In contrast to the behavior of ductile metals described in this investigation, brittle materials can be comminuted much more readily by ball milling in practically any medium, although some media are more effective than others in this respect (ref. 8). It is quite possible that some brittle metals may behave in the same manner. Thus, for instance, electrolytic chromium can be hammer-milled into coarse power readily because it is brittle. This chromium powder, as shown in a previous investigation by the author (ref. 6), eventually becomes workable, as indicated by its assuming a flake shape during ball milling. This indicates that some metals like chromium are brittle down to a certain (undetermined) particle size and ductile below this size. Probably this brittle to ductile change on reducing the particle size is associated with impurities in grain boundaries or in crystal imperfections in which case the metal would become ductile when the particle size reached about grain size (or a size of the order of the dimensions of the metal crystal between imperfections). From the writer's experience on ball milling of relatively brittle chromium in vacuum or in inert gases, its particle size can be substantially reduced. But even after long milling time periods (up to 800 hr) in what appears to be unreactive atmospheres, the ultimate particle size attainable is of the order of only 0.5 micrometer, as contrasted to 0.06 micrometer,

obtained by ball milling the same powder in water for 384 hours (see table II). It is note-worthy that, during the ball milling of the chromium in argon, the ball mill was opened several times (in an argon glove box) to examine the powders, and the mill was refilled with argon. Hence, the reaction of residual gases (oxygen, carbon monoxide, carbon di-oxide, and nitrogen) in the argon with the chromium may have contributed to its comminu-tion. Quite probably, the ultimate particle size obtainable by ball milling more ductile materials (such as nickel, e.g.) in truly inert atmospheres is much larger than that ob-tained for chromium.

It has been theorized by Rehbinder (ref. 9) that adsorption of liquids or surface ac-tive agents at structural defects (microcracks) on the surface of metals reduced their re-sistance to rupture. This weakening of the metal at structural defects was ascribed to the sharp reduction in the surface energy of the metal by the adsorbate. This theory could account for the increased friability of brittle material or structurally weak metals ball milled with liquids or with surface active agents. Most of the energy required to propagate a crack in a ductile metal, however, is used up in plastic deformation at the crack tip and is about 30 times larger than the surface energy created by propagation of the crack (ref. 14). This fact implies that, on ball milling ductile metals and alloys, the lowering of their surface energy by liquids or surface active agents should make little difference in their friability. Probably, in most cases, the liquids, surface active agents, and other additives used in ball milling aid comminution by preventing welding of particles rather than by aiding crack propagation.

One of the possible mechanisms by which particles could fracture on ball milling in reactive media can be described from thermodynamic considerations. Ball milling cold works the metal particles, and cold working makes the metal more reactive. The cold working of the particles is most severe in the volume of each particle caught between im-pacting balls (or between balls and ball-mill wall) and this volume acquires a lower (i.e., more negative) free energy of reaction than the rest of the particle. In addition and on the average, the points of impact in the particle become thinner than the rest of the particle and the surface area of the particle is stretched the most. For these reasons, the im-pacted regions of the particle are more reactive with the ball-milling medium while the rest of the particle either does not react or reacts to a lesser extent because its surface remains protected by a previously formed reaction coating. Thus, the eventual fracture of the particles probably occurs through these most cold-worked regions, both because they are thinner (hence, weaker) than the rest of the particle and because the localized chemical reaction produces a weaker (and probably also deeper) brittle reaction coating. It might be thought that the balls are very large compared with the particles and that, hence, these particles should be uniformly flattened and cold worked by impact of the balls. Actually, however, the balls are not perfectly smooth but have microscopic ridges which could cause localized cold working of the particles. In addition, and as pointed out

by Rose and Sullivan (ref. 8, p. 221), some particles of the material being milled are driven into the surface of the balls. The protruding part of the embedded particles could then cause the localized cold working of the other particles being impacted.

Welding of particles during ball milling. - Concurrently with particle fracture there is a competitive process of particle welding taking place during ball milling. There are at least two aspects to the avoidance of particle welding: first, to keep the submicron particles dispersed in the milling fluid, such as by ionic charges (ref. 15), by proper additions to the milling fluid (refs. 5 and 8), by stirring, etc., and second, to avoid their welding when they do touch.

In their work on the nature of friction in metals, Bowden and Leben (ref. 12) showed that metals can be welded by frictional energy. Bowden and Moore (ref. 16) showed, further, that welding of metals can take place even when the surfaces of the metals are lubricated (after rupture of the lubricating film). The driving force for this metal to metal welding is the change in total surface energy of the metal.

With the preceding facts in mind, it should be relatively easy to visualize how particles of ductile metals become welded to each other during ball milling in nonreactive media. Particles of submicron size dispersed in a liquid tend to stick together when they touch each other (ref. 15). The loose agglomerates of particles thus formed can become welded together when caught between impacting balls. Other things being equal, the smaller the particles the more easily they stick together. As the particles grow by welding, they may eventually reach an equilibrium size at which the rate of welding equals the rate of fracture.

When reaction between the metal particles and the ball-milling medium occurs, the surface of each particle becomes coated with a film and the metal to metal contact between coalescing particles ceases. If the reaction product on the surface of the particles is an oxide, the surface may be negatively charged, because the oxygen ions are of much larger size than metal ions (ref. 17). This charge would reduce the "stickiness" or cohesive force of the particles (ref. 15). Thus, particles can still agglomerate, but with more difficulty, hence reducing the welding rate. Other factors that act against welding of particles with oxide (or other compound) coatings are that the surface energy of compounds is generally smaller than that of the corresponding metals and that welding oxide to oxide may require fairly close pairing of the cations in one surface with the anions in the other. Although oxide to oxide welding can occur (ref. 13) and it is also possible that metal-metal welding of oxidized particles could occur by rupture of the oxide skins (ref. 18), it is evident that whatever the type of welding for oxide-coated particles, this welding will be much more difficult than for uncoated particles. On the other hand, particle fracturing would be aided by chemical reaction. Hence, the equilibrium particle size of the particles coated with reaction products should be smaller.

The extent to which the welding of particles is influenced by reaction with the grinding medium depends, to a degree, on the nature of the reaction product formed. Some of the reaction products formed on the surface of the powders may be soft, or nonadherent, or soluble in the ball-milling medium. These factors would act against extensive comminution because all three processes would tend to produce exposed metal surfaces and hence enhance metal to metal welding. On the other hand, a porous but adherent coating may enhance comminution by deterring welding. Thus, for instance, if on ball milling in pure water a porous oxide (or hydroxide, or hydrated oxide) is formed, reaction of water with the underlaying metal may continue long after the surface is first formed. In this case, the hydrogen being evolved would tend to further reduce welding, since the hydrogen pressure buildup at the interface between particles would push the particles apart.

Extension to other systems. - Although the experiments reported herein were conducted only with water or with oxygenated water as the grinding media, the previous arguments are believed to be valid for most types of coating which may be formed on metal particles by reaction with the grinding media. Hence, reactive gases, or solids, either alone or dissolved in nonreactive liquids, or reactive liquids could prove to be good grinding media.

Impurities from Reaction During Ball Milling

An interesting factor in any comminution process is the cleanliness of the final, ground product. In particular, in the case of metals it is desirable to produce powders with high specific surface area and low oxygen. The oxygen reacted with the powders ball milled in pure water (zirconium, tantalum, 430 stainless steel, and iron) as a function of ball-milling time are plotted in figure 10. The data points for these curves were
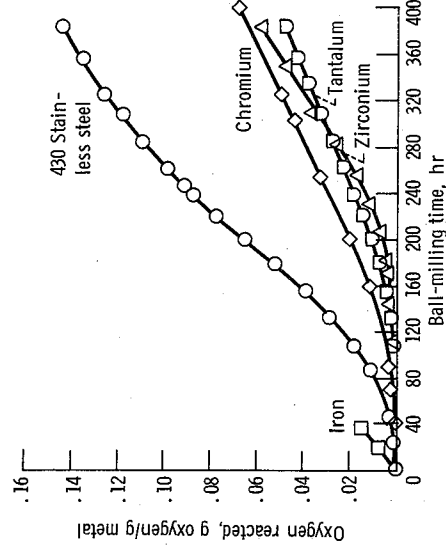

Figure 10. – Oxygen reacted with metal powders on ball milling in pure water as function of ball-milling time.

calculated from the pressure built up in the mills (due to hydrogen evolution) by equations (A2) and (A3). The corresponding curve for chromium (from ref. 6) is included in figure 10 for comparison.

The oxygen reacted with the metals ball milled in oxygenated water as a function of ball-milling time are shown in figure 11. Only the curves for copper and nickel are shown in this figure since, as already indicated, silver did not react with oxygen to any appreciable extent. The data points for the curves in figure 11 were obtained from the pressure decrease during ball milling (fig. 4 for nickel and fig. 5 for copper) and equation (A4).

The ratio of oxygen combined ΔW to increase in surface area ΔS is a measure of contamination of the powders during ball milling. The smaller this ratio, the lower the amount of oxygen combined with the powder for a given particle size. These $\Delta W/\Delta S$ ratios are listed in table V. The values of ΔW used are the last points from each of the curves in figures 10 and 11. The ΔS values were obtained by subtracting the surface areas of the as-received powders in table I from the as-milled surface areas in table II. Those metals that could not be comminuted were not included in table V because for them the $\Delta W/\Delta S$ ratio is meaningless. Furthermore, it should be noted that zirconium, and perhaps tantalum, formed hydrides (in addition to oxides) during ball milling. Obviously, the hydrogen used up in forming the hydrides did not contribute to the pressure built up in the ball mill and, for this reason, the $\Delta W/\Delta S$ ratios for these two metals are probably larger than indicated in table V. It is surmised from the slopes of the curves for zirconium and tantalum and by comparison with the results for chromium (in the same fig. 10) that the $\Delta W/\Delta S$ ratios could be about half those stated in table V. It is clear that when ductile powders are comminuted by a process that involves reaction with the milling media, the resulting powders may contain large quantities of impurities.
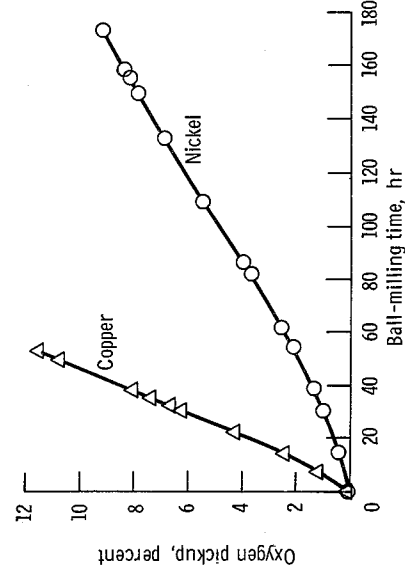

Figure 11. - Oxygen reacted with copper and nickel ball milled in water pressurized with oxygen as function of milling time.

TABLE V. – RATIO OF INCREASE IN OXYGEN CONTENT TO

INCREASE IN SURFACE AREA

Metal or alloy	Ball milling in pure water		Ball milling in water pressurized with oxygen	
	Ball-milling time, hr	Ratio of increase in oxygen content to increase in surface area, $\Delta W/\Delta S$, g/m^2	Ball-milling time, hr	Ratio of increase in oxygen content to increase in surface area, $\Delta W/\Delta S$, g/m^2
Zirconium	384	49×10^{-4}	-----	--------
Tantalum	384	127	-----	--------
Chromium[a]	384	67	-----	--------
Iron	38	47	-----	--------
Stainless steel, type 430	384	17	-----	--------
Nickel	174	--------	174	128×10^{-4}
Copper	205	--------	52.5	33
Silver	237	--------	237	--------

[a] Data from ref. 6.

CONCLUDING REMARKS

From the results of this investigation it has been hypothesized that for extensive comminution to occur during grinding of ductile metals and alloys they must react with the grinding media. The particle size of the powder obtained after a given grinding time will depend on the rates of particle fracture and of particle welding which occur concurrently during grinding; the larger the fracture rate or the smaller the welding rate, the finer the resulting powder. It is suggested that reaction aids comminution both by decreasing the strength of the particles at the points of impact with the balls and by forming a coating on the particles that hinders welding.

It follows from the preceding results that when reaction of the metal or alloy powders with the grinding media during ball milling is required for extensive comminution, other reactive gases, liquids, or solids either alone or dissolved in (nonreactive) liquids could prove to be good grinding media.

According to the stated hypothesis (that extensive comminution of ductile metal powders requires reaction with the grinding media) the resulting ultrafine powders will be contaminated with the reaction products, often to high levels. Hence, the resulting powders must either be cleaned before use or else used in applications where the coating is

not detrimental. Depending on the intended application of the powder, a grinding medium should be chosen that produces small amounts, or easily removable, or harmless (or perhaps even useful) reaction products.

SUMMARY OF RESULTS AND CONCLUSIONS

This investigation was conducted to determine the behavior of metal powders on ball milling either in pure water or in oxygenated water and from this to gain an insight into the grinding mechanism. The results and the conclusions drawn therefrom can be summarized as follows:

1. It is hypothesized that for extensive comminution of most ductile metal or alloy powders to occur during grinding they must react with the grinding media. This conclusion is based on the following experimental observations:

a. Zirconium, tantalum, iron, and an alloy (type 430 stainless steel) became extensively comminuted when they were ball milled in pure water. They also reacted with water during ball milling, and hydrogen was released. Nickel, copper, and silver could not be comminuted by ball milling in pure water. These metals did not react with water during ball milling. Thus, when metals or alloys reacted with water on grinding they were comminuted, but when they did not react with it they were not comminuted. Which metals may react with water during ball milling can apparently be predicted because those metals that reacted had oxides with more negative free energies of formation than that of water.

b. Nickel, copper, and silver were also ball milled in oxygenated water. Nickel and copper became extensively comminuted during ball milling and reacted with the dissolved oxygen. Silver neither reacted with the dissolved oxygen nor was it comminuted. Again, when no reaction occurred there was no comminution. Also these reactions can generally be predicted from free energy considerations. Silver did not react with oxygen appreciably probably because the free energies of formation of its oxides are relatively small.

c. X-ray diffraction analyses of the powders that could be comminuted by ball milling showed the presence after comminution of either oxides, hydroxides, or (for zirconium and perhaps for tantalum) hydrides. X-ray diffraction analyses of the powders that could not be comminuted showed only the pure metal.

2. When no comminution occurs on grinding, the surface area of ductile metal powders may still grow slightly by flattening of the metal particles, or decrease by welding of particles with each other.

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3. The interfaces between the particles that become welded on grinding have pockets or pores that may trap the ball-milling media and thus contribute to the contamination of the ball-milled powders.

Lewis Research Center,

National Aeronautics and Space Administration,

Cleveland, Ohio, June 11, 1968,

129-03-01-05-22.

APPENDIX - PROCEDURE USED FOR CALCULATING OXYGEN REACTED

WITH METAL POWDERS

Ball Milling in Pure Water

The writer has shown that, on ball milling chromium in water, hydrogen was released causing a buildup in ball-mill pressure (ref. 6). Except for minor temperature effects, an increase in ball-mill pressure during the grinding of metals or alloys in pure water must be the result of hydrogen release. The oxygen picked up by the metal or alloy because of its reaction with water was calculated as follows.

The free volume V of the ball mill was calculated by subtracting the volume of the water, balls, and metal powder charge from that of the empty mill. The moles of hydrogen generated were then calculated from the increase in ball-mill pressure ΔP and the free volume of the ball mill:

$$\text{Moles of hydrogen} = \frac{\Delta P(\text{atm}) \times V(\text{liters})}{22.4[(\text{atm})(\text{liters})/\text{mole}]} \tag{A1}$$

For every mole of hydrogen generated, 16 grams of oxygen reacted with the metal or alloy powder. Since 150.00 grams of powder were used in all cases (except as noted) it follows that

$$\text{Oxygen picked up by metal} = \frac{\Delta P(\text{atm}) \times V(\text{liters}) \times 16}{22.4[(\text{atm})(\text{liters})/\text{mole}] \times 150} \tag{A2}$$

Also, for every mole of hydrogen generated, 18 grams of water are lost. Hence, V increases slightly during ball milling. The increase in volume ΔV is

$$\Delta V = \text{Volume of water reacted} - (\text{Volume of oxide formed} - \text{Volume of metal reacted}) \tag{A3}$$

The data in this report were corrected for this ΔV.

Hydrogen has a critical temperature of 33.1 K and a critical pressure of 12.8 atmospheres (13×10^5 N/m^2) (ref. 19). In this investigation, the hydrogen pressure never exceeded 12 atmospheres (12.2×10^5 N/m^2) and the temperature was 296±3 K. For these reasons, hydrogen was assumed to behave as an ideal gas (ref. 19) and the data obtained needed no further corrections.

Ball Milling in Oxygenated Water

On ball milling in oxygenated water, the reaction of oxygen with the metal reduced the pressure in the mill. The oxygen reacted was determined from the decrease in ball-mill pressure ΔP and the free volume of the mill (0.500 liter or 0.500×10^{-3} m^3, in all cases) by the equation

$$\text{Oxygen picked up} = \frac{\Delta P(\text{atm}) \times 0.5(\text{liter}) \times 32(\text{g oxygen/mole})}{22.4[(\text{atm})(\text{liters})/(\text{mole})] \times 150(\text{g metal powder})} \qquad (A4)$$

Oxygen has a critical temperature of 154 K and a critical pressure of 49.7 atmospheres (50.4 $\times 10^5$ N/m^2) (ref. 19). In this investigation, the temperature was 296±3 K, and the oxygen pressure never exceeded 11 atmospheres (11.1 $\times 10^5$ N/m^2). Under these conditions, the compressibility factor chart (ref. 19) shows that the deviation from ideal behavior is less than 1 percent. For this reason, no correction was applied to the pressure data obtained for the runs with oxygenated water.

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